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ACUTE TOXICITY OF SIMULATED SODA, SODA-ANTHRAQUINONE AND SODA-ANTHRAQUINONE-BORATE PULPING EFFLUENTS

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Acute toxicity of simulated soda, soda-anthraquinone and soda-anthraquinone-borate pulping effluents

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ABSTRACT

The acute toxicity and treatability of simulated bleached pulp mill effluents were evaluated for the soda, soda-anthraquinone and soda-anthraquinone-borate processes. Pulping, bleaching and biological treatment were done on a laboratory scale. No differences in treatability were observed for effluents with and without anthraquinone. Borate addition to soda pulping liquors resulted in increased color production; however, other effluent characteristics were similar for all treated effluents. Acute toxicity to fathead minnows and *Daphnia* was comparable for untreated effluents with and without anthraquinone. Untreated pulping liquor containing borate resulted in a somewhat greater effluent toxicity to fish and *Daphnia* than did the untreated pulping liquors containing soda or soda with anthraquinone. Biologically treated effluents were not acutely toxic to either organism for any of the effluents.

Keywords

Toxicity
Daphnia magna
Fathead minnow
Pimephales promelas
Soda pulping
Borate pulping
Anthraquinone
Biological treatment
Activated sludge
Bleached pulp
Pinus taeda

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Introduction

The use of anthraquinone (AQ) as an additive in soda and kraft pulping (1-5) continues to offer considerable promise as a means of improving yield and productivity. It appears likely that these improvements can be translated into economic benefits. However, these benefits can be realized only if implementation in the digester area does not necessitate major additional expenditures by creating problems elsewhere in the mill or by producing effluents with enhanced toxicity or other adverse environmental impacts.

The possibility that anthraquinone addition to the pulping process might produce toxic compounds which could threaten life in receiving streams as well as biological waste treatment systems prompted a recent comparative study of the toxicity and biodegradability of simulated kraft and kraft-AQ pulp mill effluents (6). On the basis of this study, it was concluded that the addition of 0.1% AQ to white liquor had no effect on either the acute toxicity or treatability of effluents from the kraft pulping of loblolly pine.

The kraft process was judged most appropriate for a first study of the possible effects of AQ addition on the operation of waste treatment facilities, since this mode of AQ application appears to be of most immediate interest to the pulp and paper industry. Other applications have significant potential, however, and the questions of toxicity and treatability must be considered separately for each. One other application is the soda process. Another alternative has been suggested by recent studies of autocausticizing alkaline pulping systems by Finnish workers (7-9).

Janson and Pekkala (8) have shown that, in the soda pulping of Pinus silvestris, sodium hydroxide can be replaced with sodium borate having the composition Na_2HBO_3, without effect on yield or pulp properties. The motivation for making such a replacement lies in the fact that the borate liquor is autocausticizing, i.e., it has the ability to spontaneously expel carbon dioxide upon combustion. The use of such a system could significantly reduce the capital cost of a new mill by eliminating the causticizing and lime reburning systems.

Borate pulping is similar in all respects to soda pulping, and present indications (7,8) are that it may be thought of as pulping with NaOH in the presence of an equimolar amount of $NaBO_2$, which is inert as far as the pulping process is concerned. It seems reasonable to expect, then, that AQ would have the same beneficial effects on the borate system as it does on the soda system and that the resulting process would be a relatively low-capital, low-pollution alternative to the kraft process.

Information about the environmental impact of effluents from conventional processes, such as kraft, are generally sparse. Effluent characteristics and environmental impact information for soda and soda-borate process effluents are nearly nonexistent. Information that is available on conventional effluents would lead to the conclusion that pulping, bleaching and even biological waste treatment may result in anthraquinone compounds, or combinations of anthraquinone with other compounds, which could result in increased toxicity in final effluents.

This work seeks to extend the earlier study (6) to obtain environmental impact information related to the acute toxicity and treatability of soda, soda-AQ, and soda-AQ-borate simulated effluents. These data will enhance the growing data base relative to the acceptability of anthraquinone as a pulping additive.

Procedures

Effluent preparation

Pulping of loblolly pine chips was carried out in multiple 500 mL laboratory pressure vessels which were rotated in a heated oil bath. A 4:1 liquor-to-wood ratio was used with 80 g of oven-dry loblolly pine chips (<7/8 inch) in each vessel. The cooks were repeated at weekly intervals to continually provide fresh liquor samples for toxicity and treatability testing. Cooking conditions and averaged results are given in Table I.

[Table I here]

In each case, the cooked chips were diluted to 2% consistency, fiberized in a Waring Blendor, and filtered to obtain the black liquor, which was set aside. The pulp was then thoroughly washed and the washings discarded. Chlorination and caustic extraction stages were then carried out using the conditions given in Table II and effluents from each stage were collected at 3% consistency. Washer inefficiency was simulated by carrying over 1% of the black liquor into the chlorination stage and 5% of the chlorination effluent into the caustic extraction stage.

[Table II here]

The feeds to the activated sludge reactors were prepared by mixing 2250 mL chlorination stage effluent, 2250 mL caustic extraction effluent, and 2300 mL black liquor and diluting to 76 L with dechlorinated tap water. Feed makeup was in accordance with nominal flows from unit processes for a typical mill as set forth in a recent EPA document (10).

Reagent grade NH_4Cl and KH_2PO_4 were added to provide nutrients for biological growth. Finally, the pH was adjusted to 7.5 with dilute H_2SO_4.

Simulated final mill effluents were produced by treating the feeds in 3 liter complete-mix activated sludge units. Each reactor was baffled

and mechanically stirred to ensure complete mixing. Air was metered through a water-filled gas washing bottle to minimize evaporation losses in the reactors. The reactors were fed at a rate of 9 liters/day producing a hydraulic residence time (HRT) of 8 hours. The mean cell residence time (MCRT) was controlled by daily wasting of sludge directly from the reactor. Treatment conditions are given in Table III and discussed later.

[Table III here]

The activated sludge units were operated to give conditions typical of those used in full-scale plants. A minimum dissolved oxygen of 2.0 mg/liter was maintained in the reactor while 1.0 mg/liter NH_3-N and 0.5 mg/liter PO_4-P were maintained in the effluent to prevent nutrient limitations.

The reactors were operated until a steady-state condition, as judged by stable effluent soluble COD and suspended solids concentration over time, was reached. Samples were then collected for toxicity analyses.

Toxicity analyses

The experimental effluents generated in the laboratory were tested for acute toxicity using two test organisms and three test procedures. Both treated and untreated samples of simulated pulp mill effluent were collected for toxicity testing. Untreated effluents consisted of reactor feeds collected prior to biological treatment in the activated sludge reactors. The treated effluent tested was final effluent collected following biological treatment.

Effluents were collected as generated, combined in sealed storage containers and stored in the dark at 4°C. Bioassays were conducted as soon as sufficient effluent volumes were available.

Target organisms included animals which are common to both the laboratory as well as to the natural aquatic environment. The fathead minnow (Pimephales promelas) and the crustacean (Daphnia magna) were used for bioassays. The fathead minnows were wild trapped fish obtained from a commercial supplier in southern Wisconsin. Daphnia magna were obtained from cloned cultures maintained in the laboratory. Both adult as well as early instars, which were less than 24 hours old, were used for bioassays. Early instars were cultured and collected in a funnel apparatus described by Dewey and Parker (11,12).

The three assays included static bioassays for the fish and Daphnia magna and a residual oxygen assay (ROA) for the fish. The static assays were conducted within guidelines suggested by the EPA (13). The residual oxygen assay was similar to that described by Ballard and Oliff (14) and used by Vigers and Maynard (15) as well as McLeay (16).

Fish static bioassays were conducted in 20-liter polyethylene bag aquaria (17) lined with nylon mesh netting for 96-hour duration. Fish were acclimated at least two weeks prior to testing and were unfed for 24 hours prior to and during the test. Ambient temperatures (18-24°C) were used with dissolved oxygen levels maintained by means of aeration with inverted funnels. Fish loading rates (0.49-0.6 g/L) were consistent between concentrations and between tests. Test conditions which existed during fish bioassays are described in Table IV.

[Table IV here]

Daphnia static bioassays were also conducted according to EPA guidelines (13) and were tested at the same ambient temperature conditions as the fish. Both adult and early instar Daphnia were assayed in 250 mL

beakers containing 5 Daphnia and 100 mL of solution. Test duration was 48 hours. Food was not added during the test.

Acute toxicity is expressed in this study in terms of an LC50, an EC50, or the threshold values (for the ROA data). The LC50 is the effluent concentration in % volume at which half of the test animals survived for the 96-hour test period. This is a common term and was used to express fish toxicity data. For Daphnia, death is more difficult to verify and, for this reason, the toxic response is expressed as an EC50. An EC50 is the effluent concentration at which half of the test animals exhibit the chosen effect. For Daphnia the effect was loss of locomotor responses. In almost all cases this indicates a dead or dying animal. Both the EC50 and the LC50 as well as their 95% confidence limits were calculated according to the modified Litchfield-Wilcoxin procedure (13).

The threshold value was determined for the residual oxygen assay by means of graphical extrapolation. This value is the point at which toxicity affects fish respiration. It is indicated by the presence of an oxygen residual which exceeds that of nontoxic or control solutions following death of the fish.

Results and discussion

The desired kappa number of 34 was reached after 272 minutes cooking with 20% active alkali (AA), or 25.8% NaOH. Addition of 0.1% AQ allowed simultaneous reductions in cooking time, to 174 minutes, and AA, to 17%. In the soda-AQ-borate system, the required conditions were similar.

The feeds to the treatment reactors were prepared by mixing the three unit operation effluents in the proportions reported to be typical of a model mill (10). The characteristics of these unit operation effluents

are shown in Table V.

[Table V here]

The actual characterization of the feeds to the treatment reactors is presented in Table VI. This table also presents the characteristics of the effluents which were used for toxicity testing.

[Table VI here]

Throughout the course of this study no significant operational problems were encountered. The reactors were assumed to be at steady state following a period of time equal to three times the mean cell residence time, at which point effluent quality was stable. There was essentially no difference in the achievement of a steady state between any of the reactors. There was also no meaningful difference between the final effluents with respect to BOD_5 and TSS as shown in Table VI. The addition of borate apparently produced color bodies which were highly resistant to biological attack. No significant removal of color was observed in the soda-AQ-borate system while the soda and soda-AQ systems produced substantial color removals.

Acute toxicity comparisons

Static bioassays of untreated soda and soda-AQ effluents using fathead minnows indicated rather high acute toxicity (Table VII). LC50 values of 5.0% and 6.1% were produced. The similarity of these values indicate that there was no difference in the toxicity to fathead minnows of the untreated pulping effluent due to the presence of the anthraquinone. When these effluents were biologically treated there was no acute toxicity indicated for either of the two process streams. Treated soda-AQ effluent sustained 90% fish survival in 100% effluent for the 96-hour test.

[Table VII]

Fathead minnows were also exposed to treated and untreated effluents during the residual oxygen assay. Results are presented in Fig. 1. Acute toxicity was again evident in the untreated samples but there continued to be no difference between the soda pulping effluents with or without anthraquinone. A threshold value of 14% effluent was measured for untreated soda effluents and a threshold value of 18% was determined for the untreated soda-AQ effluents.

[Fig. 1 here]

Treated effluents from all three pulping processes failed to produce a threshold value for the ROA test which indicated the lack of acute toxicity. This supports the conclusion, based on the static fish assay, that soda-AQ effluents were not acutely toxic to fish following biological treatment.

The nonfish test organisms Daphnia magna proved to be considerably less sensitive to untreated soda pulp effluents than was the fathead minnow (Table VII). Daphnia adults showed EC50 values which were substantially greater than the fish LC50 values. This means that more effluent was required to kill (or immobilize) Daphnia than was needed to kill the fish. The average EC50 value for two tests with Daphnia adults was 30.9% for soda and 47% for soda-AQ effluents. The soda-AQ effluent was the less toxic of the two.

Samples of biologically treated effluents from the soda and soda-AQ processes did not immobilize a single adult Daphnia in any of the 4 tests during the 48-hour test period nor during an additional observation period of 48 hours. Neither the soda nor soda-AQ process effluents retained acute toxicity to adult Daphnia after biological treatment.

Early instar Daphnia are more sensitive to toxicity than are the adults. These young organisms were also exposed to treated and untreated effluents from both processes. The untreated soda-AQ effluents were considerably less toxic than soda effluents. This was true for both tests. It was also seen that a wide variation existed in the response of the early instars to different samples of the two effluents.

Biologically treated soda and soda-AQ was not toxic to early instar Daphnia. Only one individual died in 100% effluent for all tests of both processes during observation periods up to 96 hours. In spite of the greater sensitivity of the early instars, biologically treated effluents from both processes were not acutely toxic.

When borate was added to the soda-AQ pulping liquor it failed to have any great affect on the toxicity of the final effluent. Untreated soda-AQ-borate, with an LC50 of 4.4%, was about as toxic to fish as the untreated soda and soda-AQ effluents. The residual oxygen assay using fathead minnows produced similar results for tests of two samples of the same effluent. The ROA threshold value was 11.7% which is about the same as the soda and soda-AQ threshold values.

Daphnia magna displayed a very consistent toxicity response to the untreated soda-AQ-borate effluent. Assays with adults produced an EC50 of 26% for two different tests of the same effluent. This indicates greater acute toxicity for the soda-AQ-borate effluent than for either the soda or soda-AQ effluents. Early instar Daphnia showed similar sensitivity as adults with a mean EC50 value of 26.5%.

Biologically treated soda-AQ-borate effluents failed to produce any sign of acute toxicity. Fathead minnows tested by static 96-hour bio-

assays showed 100% survival in 100% effluent. The residual oxygen assay showed no residual oxygen changes or toxicity threshold values for two separate assays.

Daphnia adults and early instars also showed EC50 values greater than 100%. Survival was at 90% for adults in 100% effluent after 48 hours. For early instars survival in 100% effluent was at 80% and 100% after 48 hours for two separate tests.

Conclusions

It can be concluded from this evaluation of treatability and toxicity of the effluents produced from lab scale bleached soda, soda-AQ, and soda-AQ-borate pulping that:

1. The addition of anthraquinone and borate did not affect the treatability of lab scale soda pulping effluents by biological means.

2. Neither anthraquinone nor borate caused any appreciable change in the acute toxicity of untreated effluents to the fathead minnow or Daphnia magna.

3. Following biological treatment no acute toxicity remained in either of the three effluents when assayed with fathead minnows and Daphnia magna.

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I. Pulping conditions

	Soda	Soda-AQ	Soda-AQ-borate[b]
Anthraquinone, %	0.0	0.1	0.1
Active alkali, % as Na_2O	20.0	17.0	18.0
Temperature, °C	173	173	173
Time to temperature, min	90	90	90
Time at temperature[a], min	272	174	166
Average yield, %	45.0	47.6	45.2
Average kappa number	34.2	34.4	34.0

[a]Cooking times were varied slightly from one cook to the next in order to more closely approach the kappa number target of 34. For the entire series of 5 cooks the ranges were soda 260-280 min, and soda-AQ 150-185 min. All borate-AQ cooks lasted 166 min at 173°C.

[b]Equimolar mixture of NaOH and $NaBO_2$; only the NaOH was considered active.

II. Bleaching conditions[a]

	Chlorination[b]	Extraction[c]
Chlorine, % on pulp	6.8	0
NaOH, % on pulp	0	3.4
Consistency, %	3.0	10.0
Temperature, °C	25	60
Time, min	60	60

[a]Chemical charges shown are averages. Charges used in individual bleaches were calculated from

%, Cl_2 = 0.2 x unbleached kappa no.
%, NaOH = 0.1 x unbleached kappa no.

[b]Black liquor carry over was simulated by adding back 1% of the black liquor to the washed pulp just prior to chlorination.

[c]5% of the chlorination stage effluent was added to the washed pulp just prior to caustic extraction.

III. Treatment parameters for activated sludge reactors

	HRT[a], hr	MLSS[b], mg/L	MCRT[c], days	pH	DO, mg/L
Soda	8	2468	11.1	7.2	3.3
Soda-AQ	8	2026	11.7	7.2	3.8
Soda-AQ-borate	8	2910	11.2	7.4	3.0

[a]HRT = hydraulic residence time. [b]MLSS = mixed liquor suspended solids.
[c]MCRT = mean cell residence time.

IV. Test conditions for soda, soda-AQ, and soda-AQ-borate fish bioassays

	DO, mg/L	Temp., °C	pH	Fish loading, g/L
Soda				
Untreated				
Static	1.7-7.6 (4.8)	23.7-25.0	6.5-8.8	0.6
ROA	--	23.7-24.8	7.3-8.3	3.8
Treated				
Static	2.3-10.4(4.6)	23.5-25.2	7.1-8.0	0.54
ROA	--	24-26	7.3-8.6	3.45
Soda-AQ				
Untreated				
Static	1.6-7.6 (4.8)	22.5-24.3	6.6-8.8	0.6
ROA	--	22.3-23.1	7.3-8.4	4.2
Treated				
Static	3.1-10.2(4.9)	24.0-25.1	7.1-8.2	0.61
ROA	-- --	21.5-24.0 21.1-22.9	7.6-8.7 7.3-8.6	4.0 4.0
Soda-AQ-borate				
Untreated				
Static	1.8-9.0 (7.1)	15-20	6.8-7.6	0.6
ROA	-- --	21-22 14-23	6.5-6.0 6.8-7.5	3.1 4.1
Treated				
Static	5.5-10.4(7.2)	10.5-18.0	7.2-8.2	0.49
ROA	-- --	21-22 16.9-18.0	7.1-7.9 7.5-7.9	3.2 2.9

( ) = means.

V. Pollutant characterization of pulping and bleaching unit operations

	Soda		Soda-AQ		Soda-AQ-borate	
	BOD_5, mg/L	Color, Pt-Co units	BOD_5, mg/L	Color, Pt-Co units	BOD_5, mg/L	Color, Pt-Co units
Dilute black liquor	11320	27200	10725	32500	10620	35425
Chlorination stage effluent	313	1412	348	1484	322	1225
Caustic extract stage effluent	140	6360	154	5920	120	7965

VI. Reactor feed and effluent characterization

	BOD_5, mg/L	SCOD, mg/L	TSS, mg/L	Color, Pt-Co units
Feed				
Soda	256	--	15	1122
Soda-AQ	234	--	15	1012
Soda-AQ-borate	246	--	15	1264
Effluent				
Soda	26	267	19	405
Soda-AQ	21	315	24	379
Soda-AQ-borate	26	904	29	1136

VII. Toxicity results expressed as LC50 and EC50 values in % effluent by volume

	Soda		Soda-AQ		Soda-AQ-borate	
	Untreated, %	Treated, %	Untreated, %	Treated, %	Untreated, %	Treated, %
Static fish 96 hr	5.0	>100	6.1	>100	4.4	>100
Daphnia						
Adults 48 hr	30.9	>100	47	>100	26	>100
Early instar 48 hr	10	>100	27.5	>100	26.5	>100
Residual oxygen assay (ROA) (threshold value)	14	None	18	None	11.7	None

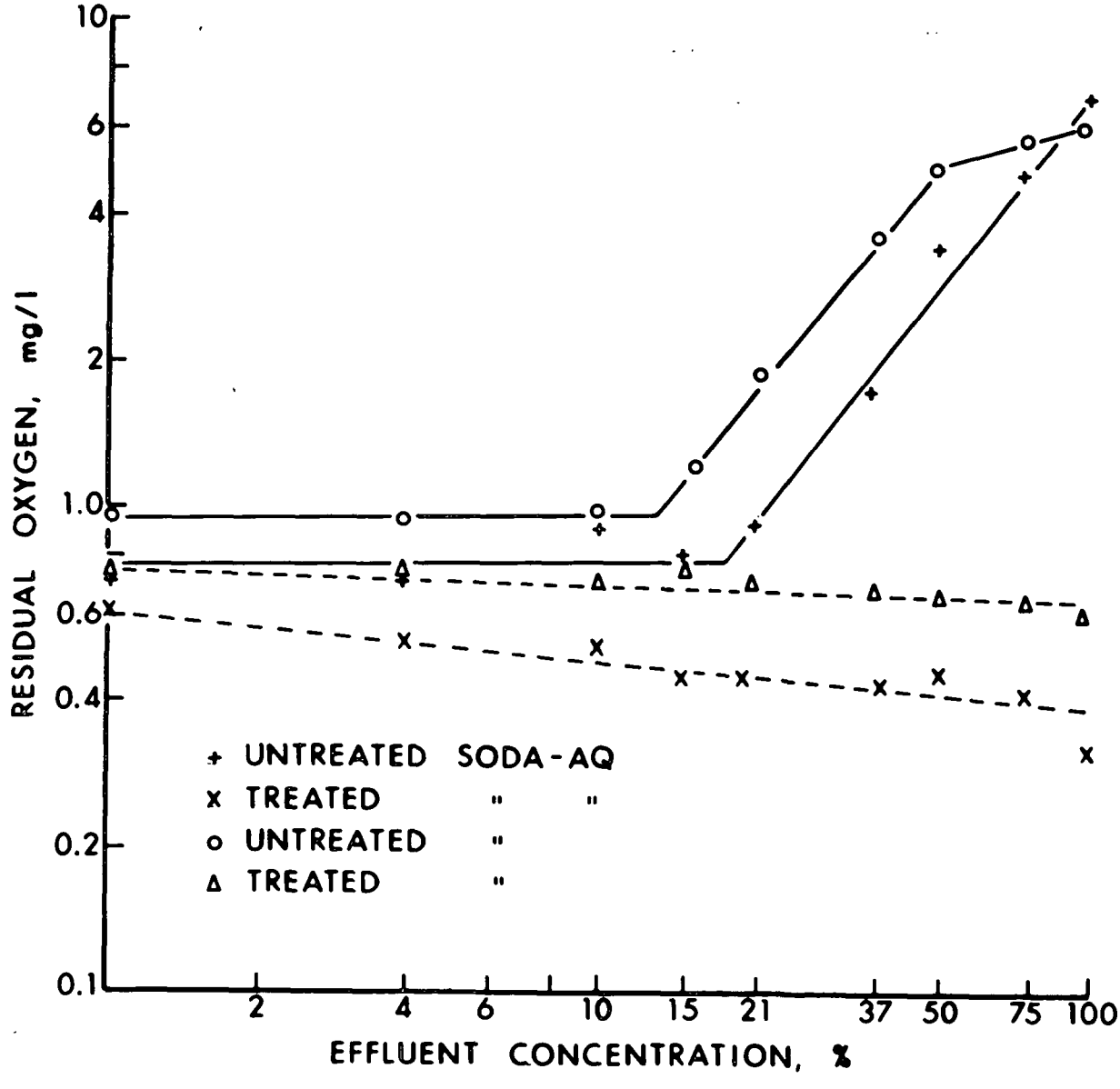

Figure 1. ROA curves for soda and soda-AQ effluents.